Landau-Zener tunneling with many-body quantum effects in crystals of molecular magnets

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We present a quantum interpretation of the heights in hysteresis of Fe_8 molecule at lower temperatures by treating the crystal as an Ising spin system with the dipolar interaction between spins. Then we apply it to two limit cases : rapid and adiabatic regions. Our theoretical analysis is in agreement with the experimental observation in these regions, which indicates that the steps in hysteresis loops of magnetization of Fe_8 at lower temperatures show a pure quantum process.

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INTRODUCTION

Crystals of molecular magnets, such as Fe_8 and Mn_{12}, have attracted much attention for their connection to many macroscopic quantum phenomena [1, 2, 3, 4]. They may also have important applications in magnetic memory and quantum computing [4, 5]. The earliest and most spectacular observation on such a system is the quantum steps in the hysteresis loops of magnetization at low temperatures [1, 4]. These quantum steps are the manifestations of macroscopic quantum tunneling, resulting from the tunneling between different spin states of large molecular spins ($S = 10$ for both Fe_8 and Mn_{12}, $S = 9/2$ for Mn_4). Fe_8 is particular interesting because the steps in the hysteresis will become temperature independent below $0.36K$, which shows a pure tunneling process [4]. This tunneling phenomenon is complicated by the interaction between spins and other environmental effects. Intensive efforts have been devoted to explain the step features via different approaches [6, 7, 8]. The modifications of other environmental effects have also been studied, such as the nuclear spin effects [9, 10, 11].

More recently, Liu, et al presented a successful theory on the height of quantum steps in the hysteresis loop when the temperature is low enough that the thermal effects can be neglected [12]. By treating Fe_8 crystal as a system of Ising spins sitting at each site of the lattice, the step heights measured in experiment were successful reproduced by directly solving an evolution equation described by the dipolar fields distribution. The results have been compared to Landau-Zener (LZ) model [13], which has been used to extract the tunnel splitting Δ of a single molecular spin from step heights [4, 14]. In their simulation, the dipolar interaction between spins is treated by a mean-field theory and the flipping of each spin is independently.

In this paper, we also model the Fe_8 crystal as a system of Ising spins sitting at each site of the lattice and taking into account the dipolar interaction between spins. But different form Ref. [12], we treat the system as a quantum many-body system and formally give a formula to evaluate magnetization. Although it can not be used to calculate magnetization in most cases for the algorithm reason (the time of calculating is increasing exponentially with the number of sites), we apply it to two limit cases: rapid and adiabatic cases. Through the pure quantum approach, our theory successfully interpret the quantum step heights in these two regions. As an application of our theory, we show that the tunnel splitting Δ_e measured with the LZ model [4, 14] is proportional to the true tunnel splitting Δ of a single molecular with a geometry factor (depending on shape and lattice structure). This result has also been obtained in Ref. [12]. In the adiabatic limit, we show the measured tunnel splitting Δ_e is dependent with the sweeping rates with the power law: $\Delta_e \sim \alpha^{1/2}$. This prediction agrees with the experimental observations.

MODEL

We model the Fe_8 crystal as spin lattices with the realistic constants $10.52 : 14.05 : 15.00$ (A) and angles $89.9° : 109.6° : 109.3°$ between the axes, which is a triclinic lattice; the shortest axis a as the easy axis (actually there is an angle of about $8°$ between them, but it does not affect significantly the results). As in Ref. [12], we focus on one step for simplicity, that is, the tunneling between the two lowest levels ($S_z = \pm 10$). The effective Hamiltonian operating in the subspace is [9]

$$\mathcal{H} = -\sum_i g\mu_B S\mu_0 H\sigma_z^{(i)} - \frac{1}{2}\sum_{ij} V_{ij}\sigma_z^{(i)}\sigma_z^{(j)} + \frac{1}{2}\sum_i \Delta\sigma_x^{(i)}. \quad (1)$$

The first term describes the Zeeman energy, and H is the external field applied in the direction of the easy axis. The second term is the spins interaction with dipolar potential $V_{ij} = E_d(3\cos^2\theta - 1)\Omega_0/r_{ij}^3$, $E_d = \frac{\mu_0}{4\pi}(g\mu_B S)^2/\Omega_0$, where $\vec{r}_{ij}$ is the displacement between the spins, θ is the angle between $\vec{r}_{ij}$ and the easy axis, and Ω_0 is the unit cell volume. The last term describes tunneling and Δ is the tunnel splitting. σ_z and σ_x are Pauli matrices, and $\{i\}, \{j\}$ label molecular sites.

Because $\Delta/E_d \sim 10^{-6}$ (see Ref. [15]), the last term of Eq. (1) can be regarded as a small perturbation, denoted as $W = \frac{1}{2}\sum_i \Delta\sigma_x^{(i)}$. We can know the eigenstates of the unperturbed system are $\phi_\mu = \mid s_1^\mu, s_2^\mu, \cdots, s_N^\mu\rangle$ ($\mu = 1, \cdots, 2^N$), in which $s_i^\mu = \pm 1$ corresponding to the spin on site i up and down respectively. The eigenvalue for ϕ_μ is

$$E_\mu = -g\mu_B S\mu_0 H\sum_i s_i^\mu - \frac{1}{2}\sum_{ij} V_{ij}s_i^\mu s_j^\mu. \qquad (2)$$

It is easy to see that the energy levels would be degenerate when some sites are geometric equivalent.

On the other hand, because $\sigma_x^{(i)}$ operating on ϕ_μ will make the spin on the i-th site flip, the perturbation term, i.e., the off-diagonal element, $\mathcal{H}_{\mu\nu} = \phi_\mu\mathcal{H}\phi_\nu = \phi_\mu W\phi_\nu$, is not zero if and only if $s_i^\mu = s_i^\nu$ ($i = 1, 2, ..., j-1; j+1, j+2, ..., N$) and $s_j^\mu \neq s_j^\nu$, where j could be any site. At this time $\mathcal{H}_{\mu\nu} = \Delta/2$.

From the perturbation theory [16], we can know, if off-diagonal element of two states is nonzero, the corresponding energy levels must have an avoided crossing with a gap proportional to the off-diagonal element $\Delta/2$. The gap of the avoided crossing is determined by the degenerate properties of the levels. For example, if both levels are non-degenerate, the gap is Δ; but if one of them is two-fold degenerate, the gap is $\sqrt{2}\Delta$, and so on. Higher order perturbations are much small, so they can be regarded as crossings. For example, for the second order, the gap is about $\Delta^2/E_d \sim 10^{-6}\Delta$, so it can be treated as a crossing.

MAGNETIZATION AND TUNNEL SPLITTING

Result of our model

Supposing the crystal has N Fe_8 molecules, it is initially on the state $\mid -1, -1, \cdots, -1\rangle$ in a large negative field, then sweep the field with a constant rate α to the positive. Over an avoided crossing, the spin involved will flip with the probability $1 - p_\delta$ where $p_\delta = e^{-\frac{\pi(\delta\Delta)^2}{2\alpha}}$ if the gap is $\delta\Delta$. The magnetization can be formally expressed as

$$\begin{aligned} M &= -NSP_{-N} - (N-2)SP_{-(N-1)} + \\ &\quad + \cdots - (N-2i)SP_{-(N-i)} + \cdots, \end{aligned} \qquad (3)$$

where $P_{-(N-i)}$ is the sum of probability for all the energy levels with i spins up. For example, assuming there are m levels of one-spin up states, which are denoted as $E_{-(N-1)}^l$ ($l = 1, 2, \cdots, m$). The energy structure is shown in Fig.1 where only the initial level E_{-N} and one-spin up levels are plotted. The energy gap between $E_{-(N-1)}^l$ and E_{-N} is $\delta_1^l\Delta$. Then we can obtain the probability of the initial level,

$$P_{-N} = \prod_l^m p_{\delta_1^l} = e^{-\frac{\pi\Delta^2}{2\alpha}c}, \qquad (4)$$

where $c = \sum_{i=1}^m (\delta_1^i)^2$. In analog, we can evaluate the probability for any level involved in principle. It can be formally expressed as

$$P_{-(N-l)} \sim \sum_\alpha \left[\prod_{\beta=1}^{l}(1 - p_{\delta_\beta})\prod_i^{m_\alpha} p_{\delta^i}\right], \qquad (5)$$

in which we have ignored some subscripts for convenience.

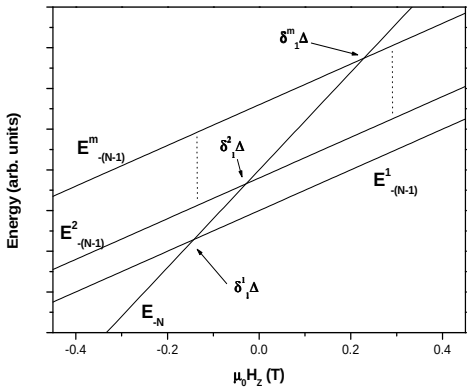

FIG. 1: The energy structure of the initial level E_{-N} and one-spin up levels. The energy gap between $E_{-(N-1)}^l$ and E_{-N} is $\delta_1^l\Delta$.

There should be a term in Eq. (3) corresponding to the adiabatic path: starting from the initial level and keeping on the continuous branch at every avoided crossing encountered. The probability of the adiabatic path can be expressed as

$$P_{ad} = (1 - p_{\delta_1^1})(1 - p_{\delta_2^1})\cdots(1 - p_{\delta_K^1}), \qquad (6)$$

where $(1 - p_{\delta_i^1})$ is the probability of spin flipping over each avoided crossing and K is just the total number of the flipped spins along this path.

Indeed, (3) can not be calculated for nowaday computer when the number of spins is large. But we can evaluate it for limit cases.

For the high sweeping rate limit, $P = e^{-\frac{\pi\Delta^2}{2\alpha}} \to 1$, so $(1-P)$ is an infinitesimal. Form Eq. (5), one knows that $P_{-(N-l)}$ is as the same order as $(1-P)^l$. Hence, to the first order of $(1-P)$, the magnetization can be approximately expressed as

$$M \approx -NSP_{-N} - (N-2)SP_{-(N-1)}. \tag{7}$$

Of course, the total probability must be conserved, i.e.,

$$P_{-N} + P_{-(N-1)} + \cdots + P_{-(N-i)} + \cdots = 1. \tag{8}$$

So, to the first order of $(1-P)$, we have $P_{-N}+P_{-(N-1)} \approx 1$, i.e., $P_{-(N-1)} \approx 1 - P_{-N}$. Substituting (4) into the above formula, we get

$$M \approx -NS + 2cS\frac{\pi\Delta^2}{2\alpha}. \tag{9}$$

In Refs. [4, 14, 15], Wernsdorfer and coworkers extract the tunnel splitting Δ of a single molecular spin from the magnetization by employing LZ model [13]. Based on LZ model, the measured tunnel splitting Δ_e was calculated by the following formula [15],

$$\Delta_e = \sqrt{-\frac{2\alpha}{\pi}\ln\left(\frac{1-M/M_s}{2}\right)}, \tag{10}$$

in which $M_s = NS$.

Substituting the theoretical predication of magnetization (9) into the above formula, we obtain

$$\Delta_e \simeq C\Delta, \tag{11}$$

in which $C = \sqrt{\frac{c}{N}}$.

This result shows that for the rapid sweeping rate limit, the measured tunnel splitting Δ_e is a constant, which consists with the experiment observation [15]. Eq. (11) also implies that Δ_e is not the true tunnel splitting Δ, but proportion to Δ with a factor C which is dependent only on the geometry of the sample: its shape and lattice structure. This consists with the result presented in Ref. [12].

If the sweeping rate is very small (adiabatic limit), $p_{\delta_i^j} \to 0$, so $P_{-(N-i)} \to 0$ except for the adiabatic term $P_{ad} \to 1$, so $M \to M_{ad} = -(N-2K)S$, then from (10) we obtain

$$\Delta_e = \sqrt{-\frac{2\alpha}{\pi}\ln\left(\frac{1-M_{ad}/M_s}{2}\right)} = k\alpha^{1/2}, \tag{12}$$

in which $k = \sqrt{\frac{2}{\pi}\ln\left(\frac{1-M_{ad}/M_s}{2}\right)}$. This shows that for the slow sweeping rates, the measured tunnel splitting is strongly dependent on the sweeping rate. In the adiabatic limit it shows a $1/2$ power law of the function of the sweeping rate: $\Delta_e = k\alpha^{1/2}$. This feature is first revealed in this paper.

Comparing our results with experiments

For the high sweeping rate limit, as shown in Eq. (11), the measured tunnel splitting is a constant, which consists with experimental observation. For the adiabatic region, we can calculate the measured tunnel splitting in the adiabatic limit since the number of levels involved in adiabatic path is proportion to the number of spins N. We can find the adiabatic path by following the adiabatic process: starting from the initial level and keeping the state on the continuous branch at every avoided crossing encountered. In Fig. 2, we plot the adiabatic magnetization M_{ad} of $n \times n \times n$ lattice for different total number of spins. One can find that as the total number of spins is large enough, M_{ad} becomes independent on the total number, and tends to a constant $M_{ad}/M_s \simeq -0.29$, i.e., $k = 0.528$. We also calculate M_{ad} for the case of $(a \times b \times c) : 16 \times 8 \times 8$ lattice (a is easy axis direction), and obtain $M_{ad}/M_s = -0.37$, i.e., $k = 0.49$. In Fig. 3, we compare the theoretical evaluation with the experiment observation [15]. It is shown that for three different Fe_8 isotopes, the three curves of Δ_e tend to merge together with the same tendency $\Delta_e \propto \alpha^{1/2}$. This tendency consists with our theoretical prediction. We argue that the adiabatic evolution of the system is only determined by the levels structure, so we cannot read the information of the tunnel splitting from the adiabatic process. This feature can be found in Fig. 5 where three curves of different isotopes have the same tendency.

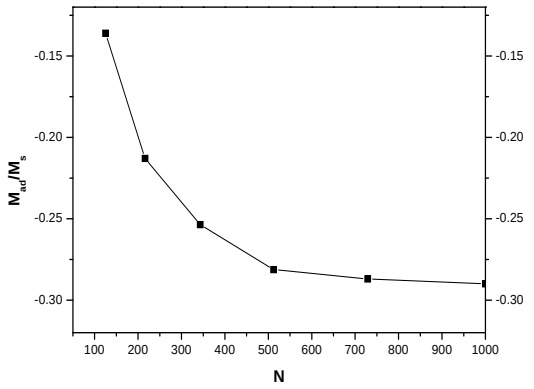

FIG. 2: The adiabatic magnetization of $n \times n \times n$ Fe_8 triclinic crystals for different number of spins. The solid line is guide for eyes. $N = n \times n \times n$ is the total number of spins.

CONCLUSION

In summary, we have given a pure quantum interpretation of the step heights in hysteresis loops of Fe_8 molecule by treating the crystal as a system of Ising spins sitting

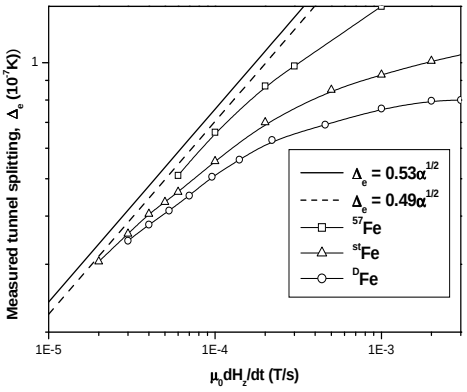

FIG. 3: Δ_e of Fe_8 crystals for small sweeping rates. The solid line is theory prediction with $n \times n \times n$, the dashed line is for $2n \times n \times n$, the others are the experimental data for different Fe_8 isotopes [15].

at each site of the lattice with the dipolar interaction between spins. Our theoretical analysis is in agreement with the experimental observation in the rapid and adiabatic limits. For the rapid sweeping rates, we show that the measured tunnel splitting Δ_e is a constant which is proportional to the tunnel splitting of the single molecular spin, i.e., $\Delta_e = C\Delta$. The factor C depends on the sample geometry. But for the adiabatic limit, the magnetization becomes independent on the sweeping rate, and tends to a constant. This feature leads to that the measured tunnel splitting Δ_e is strongly dependent on the sweeping rate α, and be a $1/2$ power law of sweeping rate: $\Delta_e \sim \alpha^{1/2}$.

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